

Hydrocarbons Analysis in Puerto Rico 2001



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Abstract

Air samples were taken in 19 locations in Puerto Rico between March and April of 2001. The samples were analyzed to study the presence of hydrocarbons in Puerto Rico due to anthropogenic and biogenic emissions. This work will help computer modelers and atmospheric scientists decide were to take air samples and were to perform meteorological analysis on the Puerto Rico 2003 Field Study.



Ozone Formation

The photolysis of NO_2 is the most important reaction in the formation of ozone:

(1)
$$NO_2 + \hbar \nu \rightarrow NO + O$$

(2) $O + O_2 \rightarrow O_3$

Small quantities of $\mathbf{0}_3$ are formed in reactions1and 2, because ozone reacts with NO to regenerate \mathbf{NO}_2 .

(3)
$$0_3 + NO \rightarrow NO_2$$
 (fast)

Introduction (Cont.)

The key species that makes ozone concentrations so high in urban areas are the OH radical and hydrocarbons (RH). They both react to form alkyl peroxy radicals (RO₂•).

(4) RH + OH•
$$\rightarrow$$
 R• + H₂O
(5) R• + O₂ \rightarrow RO₂•

The peroxy radicals react rapidly with NO to form NO₂ without consuming ozone.

$$RO_2 \bullet + NO \rightarrow RO \bullet + NO_2$$



Non-Methane Organic Compounds (NMOC's)

The NMOC's that were analyzed in Puerto Rico are:

- Alkanes-Important in the formation of alkyl peroxy radicals
- Alkenes- Constituents of gasoline fuels and vehicle emissions, are important in the formation of ozone.
- Aromatics- Are also constituents of vehicle emissions and are important in ozone formation.



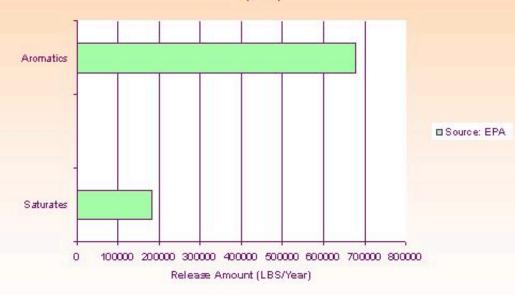
Why study Puerto Rico?

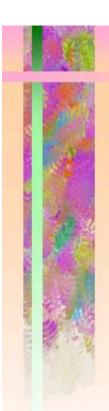
- 3.5 million inhabitants contribute to hydrocarbons and NO_x emissions from motor vehicle exhaust and stationary sources.
- Island's regular meteorology make it suitable for simplification of boundary layer conditions.
- To prove that ozone formation is possible in great amounts in an island.
- Study the formation of aerosols due to the presence of sea salt and hydrocarbons.



Fig 1. Stationary Sites Chemical Releases to Air in San Juan.

Chemicals Released to Air in San Juan From Various Industries. (1999)





Sampling and Detection Methods

- Between March and April of 2001 19 air samples were taken in Puerto Rico: two in San Juan and 17 others around the island.
- Air samples were collected in stainless steel canisters whose surfaces have been passivated (polished) in a process called SUMMA.
- The samples were analyzed using a cryogenic pre-concentration/high resolution gas chromatography technique with a flame ionization detector.



Data Analysis

- After the air samples were passed through the GC a chromatogram was produced with the peaks of all the hydrocarbons.
- I used the computer program HP Chem. Station to obtain the area of each individual peak and then used the retention times to identify each compound.



Calculations of the Hydrocarbons

- NMOC Mixing Ratios in ppbv
- NMOC Ratio is used to determine the age of the air mass.
- OH Reactivity- Is used to estimate the contribution of the hydrocarbons to the production of ozone.
- Propene equivalents- Used to normalize the OH reactivity values in terms of propene.



Fig 2. Total NMOC's (ppbC)



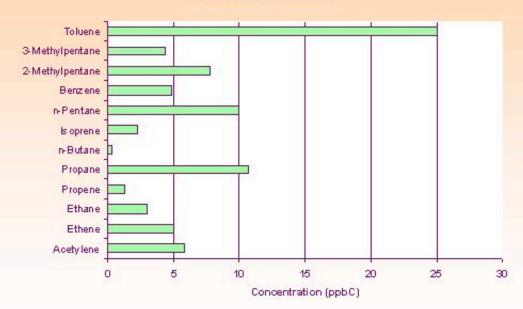
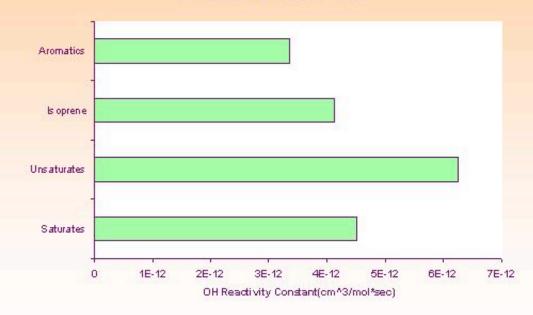




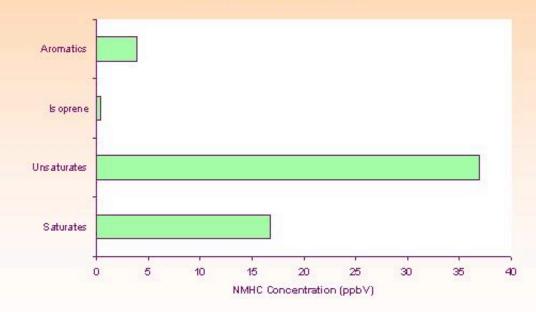
Fig 3. OH Reactivity

San Juan 3/22/01/ Time: 11:10





San Juan 03/22/01 Time: 11:10



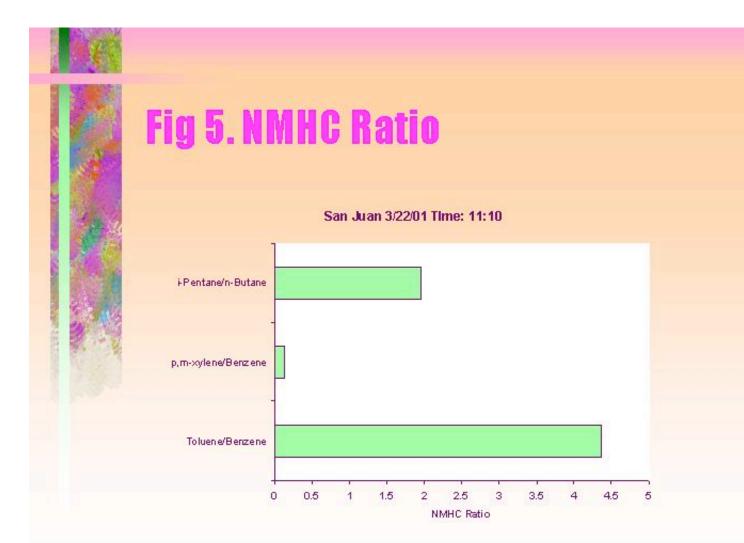


Fig 6. Propene Equivalents Aromatics ls oprene ■ Mexico City □ San Juan Uns aturates Saturates 30 Propene Equivalents(ppbv)

Conclusions

- Figures 2 and 4 indicate that considerable amounts of hydrocarbons are found in San Juan area.
- The propene equivalence data (Fig 6) indicates that hydrocarbons contributes to ozone formation significantly since saturated and unsaturated NMHC's were found in the same order of magnitude as in Mexico City.
- A more comprehensive air quality study must be performed to understand why so much ozone can be formed a small island.



References and Acknowledgments

References

 Gaffney, J.S., N.A. Marley, and R. Ravelo, 2000. Puerto Rico - 2002: Field Studies To Resolve Aerosol Processes. Symposium on Atmospheric Chemistry Issues in the 21st Century, American Meteorological Society.

Acknowledgments

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